Flexible Manufacturing of Colloidal Quantum Dot Solar Cells via Spray-Casting Techniques

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Abstract — **Colloidal quantum dots are a promising candidate material for solar energy generation because of their band gap tunability and solution-based processing flexibility. However, conventional colloidal quantum dot solar cell fabrication techniques are still limited by their lack of scalability, environment conditions, and difficult installation scenarios. Here, we develop spray-casting manufacturing methods for fabricating thin film solar cells, discuss the trade-off between conductivity and transmittance in transparent contact materials, and demonstrate the feasibility of spray-casting colloidal quantum dot layers. This work on flexible manufacturing methods paves the way for installing solar energy devices in a variety of novel scenarios.**

Keywords—colloidal quantum dots, spray casting, thin film solar cells

I. Introduction

Solar energy has been attracting the world's attention in recent decades due to its abundance, sustainability and environmental friendliness. It is now regarded as a significant replacement or supplement for traditional energy sources, especially in countries and areas with high solar irradiance. Expanding the feasibility of solar energy so that it can be used in more places and for more applications is a crucial challenge for society. Currently, the most popular and widely used solar energy conversion devices are silicon solar cells, which are highly commercialized and occupy the majority of the terrestrial solar market. Silicon solar cells, however, meet with limitations in a variety of new areas because of the heavy and rigid nature of the panels, even though their manufacturing costs have been continuously decreasing. For example, their application in building-integrated photovoltaics, major transportation methods, and mobile devices are quite limited. Additionally, the lack of mechanical flexibility makes it difficult to deploy silicon solar cells in wearable devices or on vehicle surfaces.

In order to deploy solar energy in these new applications, novel materials are needed. Colloidal quantum dots (CQDs) are thought to be one of the most promising candidate materials for thin film solar cells because of their solution-based processing capability. Critically, since the band gap of quantum dots can be tuned by varying their sizes, it is possible to fabricate multijunction solar cells using colloidal quantum dots with different sizes in both hybrid and single-material scenarios [1]. Moreover, colloidal quantum dots have high absorption in the infrared region [2], [3]. Thus, they can be important supplements to current conventional silicon solar cells which apply for the visible range better. However, in practice, the scalable fabrication of colloidal quantum dot solar cells must overcome certain limitations before they can be deployed commercially. Currently the best-performing cells use high-temperature-processed transparent conductive oxides (TCOs) which restrict the conditions of fabrication. In addition, non-portable and non-scalable spin-casting techniques are used in depositing the colloidal quantum dot absorbing layer and charge transport layers, while a vacuum environment is required for the physical evaporation of the top and bottom electrodes. These factors limit the fabrication process of conventional colloidal quantum dot solar cells to the laboratory environment.

The demands of flexible applications inspires the goal of building a colloidal quantum dot solar cell in which all layers can be fabricated via inexpensive manufacturing methods in ambient environmental conditions. Compared with traditional spin-casting processes, slot die coating processes or evaporation techniques, spray-casting shows the potential to fulfill this requirement because of several advantages for flexible thin film solar cell manufacturing. First, the starting liquid ink material has a higher utilization rate in a spray-casting process, while quite a large fraction is wasted during spin-casting [4]. Second, while spin-casting processes are limited in substrate size and require a rigid substrate, spray-casting processes have fewer limitations in terms of substrate sizes and types. Third, the use of room-temperature silver nanowire inks for the electrodes instead of bulk metal oxides and gold removes the requirements of time, temperature, pressure, and manufacturing costs for the electrodes and allows solar cells to be fabricated on almost any type of surface, expanding their feasibility in actual applications.

II. Methods, Results And Discussion

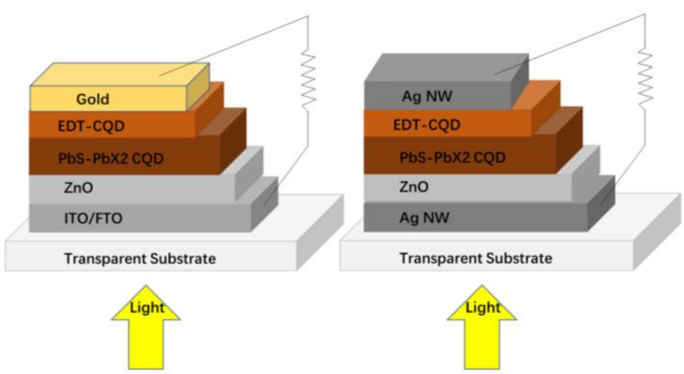

Fig. 1. (Left) Schematic of a conventional colloidal quantum dot solar cell structure and (right) a fully spray-cast colloidal quantum dot solar cell structure. EDT-CQD refers to the ethanedithiol-treated hole transport layer. $PbS-PbX_2$ CQD refers to the $PbI_2/PbBr_2$-treated light-absorbing layer. ZnO refers to the zinc oxide electron transport layer. ITO (indium tin oxide) and FTO (fluorine doped tin oxide) refer to the transparent conductive oxides. Ag NW refers to the silver nanowire-based transparent electrode.

In this work, we discuss the use of spray-cast manufacturing in building a fully spray-casted flexible CQD solar cell. Differences between the structures of a conventional CQD solar cell and a fully spray-cast CQD solar cell are shown in Figure 1. Generally, the crystalline TCO bottom electrode layer and the physically evaporated gold top electrode layer are both substituted by spray-cast silver nanowire electrode films. The zinc oxide (ZnO) electron transport layer and lead sulfide (PbS) CQD layers are all spray-cast in between the silver nanowire electrode layers. Hence, all layers of the CQD solar cell structure can be solution processed, and therefore, be spray-cast under ambient conditions.

Our work is based on the custom-built spray-casting setup shown in Figure 2. The use of a liquid siphon nozzle removes the requirement of an external liquid pressure supply. The air flow is able to trigger the liquid siphon effect, which pushes the solution into the nozzle, and the spray-casting process commences. The pilot air is set for controlling the on and off function of the spray nozzle. In this setup, we can control the quality of the spray-casted film by modifying the air supply pressure level, the height difference between the solution holder and the nozzle, the spray duration, and the number of spray cycles.

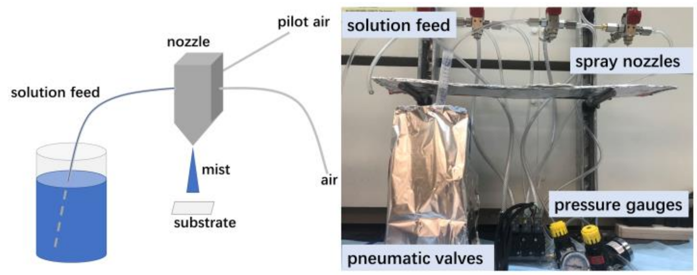

Fig. 2. Schematic (left) and photograph (right) of the spray-casting instrument. Air is supplied to trigger the siphon effect that pushes the liquid solution into the nozzle, and the spray-casting process commences. The pilot air switched by pneumatic valves which are used to turn on/off the nozzle.

A. Silver nanowire layer optimization

Silver nanowires are chosen as a substitute for conventional high-temperature-processed crystalline TCOs and evaporated metal contacts. Silver nanowires are solution-based and can be deposited under room temperature and ambient pressure conditions. The conductivity of a silver nanowire film is provided by the interconnection between single wires, while the transparency comes from the sparsity of the nanowire coverage. As in most transparent conductors, there is a trade-off between the conductivity and transparency of silver nanowire films. Our goal is to produce a film which provides sufficient conductivity for current collection in a solar cell while maintaining sufficient transparency for incident light collection.

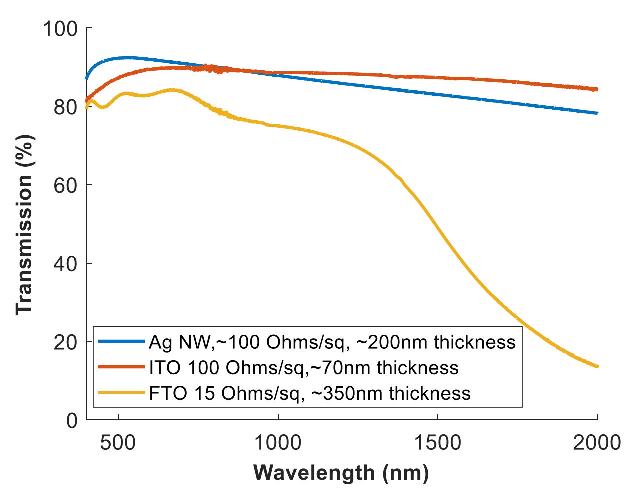

Fig. 3. Transmission curves for the best-performing spray-cast silver nanowire electrode and transparent conductive oxide control samples.

In this work, we use a silver nanowire solution provided by NanoDirect (5 mg/mL, ~20 nm diameter, ~30 µm length, dissolved in isopropanol) as our starting transparent conductor material. We find that diluting the solution to 0.5 mg/mL and annealing the film for 30 minutes after spray-casting leads to the best-performing films. The sheet resistance of the silver nanowire electrode is measured using a four-point-probe setup, and the transmittance is measured using a Cary 5000 UV-VIS-NIR spectrophotometer. Figure 3 illustrates that the best-performing spray-cast silver nanowire electrode provides transparency comparable to traditional transparent conductive oxides such as indium-doped tin oxide (ITO) and fluorine-doped tin oxide (FTO) in the visible range while maintaining an acceptable conductivity.

B. Absorbing layer optimization

After spray casting the ZnO electron transport layer [5], we moved on to developing spray-casting procedures for the PbS CQD absorbing layer. Oleic acid (OA) ligand capped PbS colloidal quantum dots are synthesized via previously published methods [6]. A solution-phase ligand exchange is performed using PbI_2, $PbBr_2$ and ammonium acetate in dimethylformamide (DMF) to get $[PbX_3]^-/[PbX]^+$-capped PbS colloidal quantum dots. This solution-phase ligand exchange increases the interconnection and decreases electronic trap state density in the CQD films. The ligand-exchanged quantum dots are then dispersed in butylamine for spray casting.

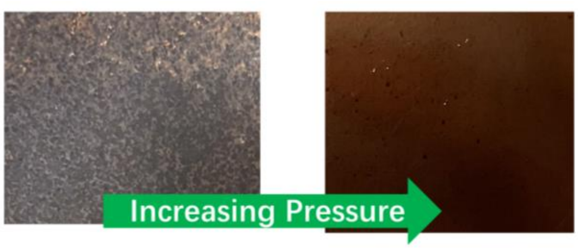

Fig. 4. Effect of spray-casting pressure on the quantum dot absorbing layer film quality.

Figure 4 demonstrates the effect of carrier gas pressure in the spray casting process. As pressure decreases, droplets are less atomized leading to a very rough film surface. Therefore, high pressures (approximately 3 bar) are needed to ensure a uniform film and shorter drying time. We also find that a high solution concentration is needed to produce smooth, high-quality CQD films. However, islands begin to form at concentrations exceeding 60 mg/ml, likely due to quantum dot aggregation [7].

C. Discussion and ongoing work

We demonstrated spray-casting processes for the silver nanowire transparent conductor layer, the zinc oxide electron transport layer and the PbS CQD absorbing layer in a PbS CQD solar cell. The remaining tasks with regards to those materials include optimization of the film smoothness and integration into full solar cell devices. The next task has the goal of developing spray-casting processes for the CQD hole transport layer, in which deposition strategy development for the solid-state ligand exchange required for the hole transport layer will be the priority.

III. Summary

In this work, we demonstrate spray-casting processes for silver nanowire films to be used as transparent conductors in PbS CQD solar cells with an acceptable combination of electrical conductivity and optical transmittance, and the PbS CQD photovoltaic absorbing layer. This proof-of-principle demonstration should enable the flexible deployment of solar energy technologies on a variety of surfaces, especially in remote locations. A fully spray-cast CQD solar cell is under development and the processes developed for that will be scaled up for flexible solar cell manufacturing and other potential solution-processed optoelectronic technologies.

IV. Acknowledgements

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